XVII. *On the Action of Nitric Acid on various Vegetables, with a more particular Examination of* Spartium scoparium, *Linn., or Common Broom.*
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THE last paper which I had the honour of presenting to the Royal Society contained an account of the effects produced by the action of sulphuric and hydrochloric acids on the *matière incrustante* of several plants belonging to the different great classes of vegetables. In the present paper I intend to describe the effects of nitric acid upon a variety of vegetable groups ; these researches having been undertaken in the hope that, by means of this powerful reagent, some light might perhaps be thrown on peculiarities in their respective constitutions.

Populus balsamifera.

The first plant experimented on with this view was the *Populus balsamifera*, as representing the numerous family of the Poplars. A quantity of the branches of this, in Great Britain, very common tree, was therefore cut into small pieces and was boiled with water till it was completely exhausted. The dark-coloured bitter-tasted liquid which it yielded was evaporated to the state of an extract. This extract was then digested with dilute nitric acid for about four and twenty hours. A great deal of nitrous fumes were given off, together with a small quantity of an agreeably smelling aromatic oil. The strongly acid solution was evaporated to dryness on the waterbath, so as to drive off as much of the adhering nitric acid as possible. The dried residue was next dissolved in a considerable quantity of hot water, and after being allowed to cool, was carefully filtered through a cloth. The clear liquid was then concentrated by cautious evaporation, and exactly saturated in the cold with carbonate of potash, great care being taken not to add an excess of the alkali. A yellow sediment soon began to appear, and its amount was greatly increased in the course of a few hours. It consisted of nitropicrate of potash and of the potash salt of a new acid, to which I have given the name of nitropopulic acid. The mother-liquor contained a great deal of oxalate and nitrate of potash. The mixed precipitates were then collected on a filter and dried by pressure, so as to remove as much of the adhering mother-liquor as possible. They were then washed with a little cold water and were treated with a cold solution of dilute carbonate of potash, which readily dissolved out the nitropopulate of potash, while it left the nitropicrate of potash unacted on. The two salts were then separated by filtration, the nitropicrate of potash remaining on the filter, while the nitropopulate of potash was dissolved in the alkaline liquid. The mother-liquor was again slightly supersaturated with muriatic

acid, when the nitropopulate of potash precipitated as a compact crystalline powder, which was collected on a filter and washed with a little cold water. It was dissolved a second time in a dilute solution of carbonate of potash, and again precipitated by muriatic acid. The object of this second treatment with an alkaline carbonate, was to remove any trace of nitropicrate of potash which might adhere to it. The nitropopulate of potash was still further purified by being digested with animal charcoal, and repeatedly crystallized out of hot water. No potash was added in these latter crystallizations, because an excess of potash, when assisted by heat, has the effect of decomposing nitropopulic acid. When, through these operations, the nitropopulate of potash has been sufficiently purified, it has merely a pale lemon-yellow colour, and may be employed for preparing nitropopulic acid. It is therefore boiled with a very considerable excess of muriatic acid, and on the cooling of the solution, the nitropopulic acid is deposited in silky needles, forming concentric groups of a pale yellow colour. Nitric acid cannot be advantageously employed for this purpose instead of muriatic acid, for, as will subsequently appear, nitropopulic acid is destroyed when it is boiled with strong nitric acid. The nitropopulic acid in this stage of its preparation is not altogether free from a small quantity of a yellowish colouring matter, which adheres to it with great tenacity. Its crystals require, therefore, to be again dissolved in dilute muriatic acid; and they are subsequently still further purified by being repeatedly digested with animal charcoal, and crystallized out of hot aqueous solutions. The crystals of nitropopulic acid, when quite pure, are perfectly colourless, and the solution from which they have crystallized has only a slightly yellowish shade. The pure nitropopulic acid requires to be pretty quickly separated from the mother-liquor by being pressed between folds of blotting-paper and immediately dried *in vacuo*, as when it is exposed to the air, even for a short time, it is very apt to become yellow. When it is deposited by slow cooling out of dilute aqueous solutions, it forms hard prismatic crystals arranged in concentric groups; but when a hot concentrated solution of the acid is rapidly cooled, it becomes filled with a mass of long slender silky needles. Muriatic acid has the effect of preventing the oxidation of nitropopulic acid, which may be readily obtained from a dilute solution of that acid in colourless crystals.

Nitropopulic acid is very soluble in water, and still more so in weak and strong spirits of wine. An addition of sulphuric or muriatic acid to its aqueous solution has the effect of considerably diminishing its solubility, and the colour of the solution becomes fainter in proportion as the amount of the mineral acid is increased. But when the acid solution is diluted with water, the yellow colour again reappears. When an excess of nitropopulic acid is boiled with dilute muriatic acid part of it dissolves, while the portion which remains undissolved melts and forms a yellowish oil, which solidifies and crystallizes when the liquid cools. Nitropopulic acid may likewise be gently heated in sulphuric acid without being decomposed, and it crystallizes again when the solution cools. When nitropopulic acid, however, is digested with pretty concentrated nitric acid, it is decomposed, being converted into nitropi-

cric acid. If nitropopulic acid is boiled with a mixture of hydrochloric acid and chlorate of potash, it is also decomposed, being changed into chloranil. When nitropopulic acid is treated with a cold solution of hypochlorite of lime, no effect is produced; and even when the mixture is treated to nearly the boiling-point, no chloropicrine is evolved; but when it has been boiled for a few minutes, a sudden effervescence takes place, and the nitropopulic acid gives off abundance of chloropicrine. This reaction is highly characteristic of nitropopulic, indigotic and chrysammic acids, and furnishes an easy test by which any of these acids may be immediately distinguished from either nitropicric or oxypicric acids, both of which evolve chloropicrine, either in the cold, or when very gently heated with hypochlorite of lime.

I must here rectify a slight error which I committed, in a short notice upon indigotic acid, which I published about two years ago. I then stated that indigotic acid might be heated with a solution of hypochlorite of lime without the production of chloropicrine. This is so far quite true; but if, as has just been stated, the mixture is boiled for some minutes, effervescence ensues and chloropicrine is abundantly evolved. Nitropopulic acid may also be easily distinguished from the above-mentioned acids by the peculiar character of its potash salt. For though, as already stated, nitropopulate of potash is very slightly soluble in pure water, it dissolves very readily in an alkaline solution, and is precipitated again when the solution is neutralized with an acid. The potash salts of nitropicric, chrysammic and oxypicric acids, on the contrary, are less soluble in alkaline lyes than they are in pure water. And indigotate of potash, though it resembles the nitropopulate of that base, in being very soluble in alkaline solutions, differs from it in being much more soluble in cold water, and in being much more easily decomposed by any of the stronger acids. Thus, when a concentrated solution of indigotate of potash is treated in the cold with a slight excess of muriatic acid, the salt is decomposed and a considerable portion of the indigotic acid is precipitated. Nitropopulate of potash, on the contrary, can only be decomposed when it is boiled with a great excess of muriatic acid. The small amount of solubility in cold water which the neutral potash, soda and ammonia salts of nitropopulic acid exhibit, is quite characteristic, and distinguishes them from the corresponding salts of indigotic acid. The taste of nitropopulic acid is very peculiar, being at first very strongly acid like oxalic acid, then astringent, and finally exceedingly bitter. Nitropopulic acid stains the skin permanently yellow. When gently heated in a retort, it sublimes and crystallizes on cooling. When strongly heated in the open air, it burns with a bright yellow flame, and when any of its salts are heated on platinum foil, they explode with considerable violence. Nitropopulic acid strikes a deep red colour with a solution of perchloride of iron. With the protosulphate of iron it merely yields a deep yellow.

The chief points which require to be attended to in preparing nitropopulic acid, may be shortly stated as follows:—The mixture of dilute nitric acid and the extract of the *Populus balsamifera*, must never be so highly heated as to boil; for if the heat is allowed to rise very high and the acid is concentrated, almost the whole of the nitro-

populic acid will be decomposed, being changed into nitropicric acid. In this respect nitropopulic acid resembles indigotic acid, which, by digestion with strong nitric acid, is also converted into nitropicric acid. When the mixture of the crude acids is dissolved in water, it must be filtered only when perfectly cold, so as to separate the resinous matter of the extract and retain it upon the filter. This resinous matter, which has usually a deep green colour when it is treated a second time with nitric acid, yields a second quantity of the mixed nitrogenated acids. It is also necessary to precipitate the mixture of the nitropicric and nitropopulic acids both together by exactly saturating them with potash, and to withdraw them from the mother-liquor before we attempt to separate the mixture of the two salts from each other; for if much resinous matter and any considerable amount of inorganic salts are contained in the solution, neither the nitropicrate nor the nitropopulate of potash readily crystallizes out of it. The mother-liquor always contains a large quantity of quadroxalate of potash and free oxalic acid, the removal of which latter substance cannot be effected by means of lime, as the basic lime-salt of nitropopulic acid is scarcely more soluble in water than the neutral oxalate of lime. It is likewise very necessary to exclude the air from nitropopulic acid as much as possible during its purification; and the dried acid should be preserved in well-stoppered bottles, as it rapidly becomes yellow on exposure to the air.

Nitropopulic acid, when dried first in the air and then *in vacuo*, loses 7·21 per cent. water. Thus 0·957 grm. lost *in vacuo* 0·069=7·21 per cent.

The nitropopulic acid dried *in vacuo*, when burned with oxide of copper and copper turnings, gave the following results:—

I. 0·323 grm. of acid gave 0·4355 CO_2 and 0·05 water.

II. 0·339 grm. of acid gave 0·455 carbonic acid and 0·058 water.

The nitrogen was determined qualitatively by LIEBIG's method.

Tubes.	Vol. mixed gases.	Vol. after absorption, or N.	Vol. of carbonic acid.
1	33	4	29
2	25	3	22
3	32	4	28
4	39	5	34
5	24	3	21
6	27	$3\frac{1}{2}$	$23\frac{1}{2}$
7	33	4	29
8	35	$4\frac{1}{2}$	$30\frac{1}{2}$
9	29	$3\frac{1}{2}$	$25\frac{1}{2}$
10	33	4	29
11	32	4	28
12	43	$5\frac{1}{2}$	$37\frac{1}{2}$
13	37	$4\frac{1}{2}$	$32\frac{1}{2}$
14	28	$3\frac{1}{2}$	$24\frac{1}{2}$
15	36	$4\frac{1}{2}$	$31\frac{1}{2}$
16	33	4	29.
17	27	$3\frac{1}{2}$	$23\frac{1}{2}$
18	32	4	28
	578	72	506

It is plain from these determinations that the nitrogen in the acid is to the carbon almost exactly in the proportions of 2 to 14 or of 1 to 7, and when calculated accordingly, they have given the subjoined result, 12·23 per cent. nitrogen.

				I.	II.
C	14	1050·00	36·84	36·77	36·64
H	4	50·00	1·75	1·71	1·79
N	2	350·50	12·30	12·23	12·23
O	14	1400·00	49·11	49·29	49·34
		2850·50	100·00	100·00	100·00

1 equivalent of nitropopulic acid dried first in the air and then

		Calculated.	Found.
in vacuo	=	2850·50=92·69	92·79
2 equivs. water		225·00 7·31	7·21
		3075·50 100·00	100·00

The formula of the acid dried *in vacuo*, as confirmed by the analysis of the potash and silver salts subsequently given, is therefore $C_{14} H_3 N_2 O_{13}+HO$, and the formula of the acid dried in the air $C_{14} H_3 N_2 O_{13}+HO+2Aq$.

Nitropopulate of Potash.

One portion of this salt was prepared by digesting crude nitropopulate of potash with animal charcoal and repeatedly crystallizing it out of water. The pure salt had a lemon-yellow colour and consisted of small prisms. It is very slightly soluble in cold water, but exceedingly soluble in alkaline solutions. A second portion of the purified salt was crystallized out of a solution which had been rendered slightly alkaline by the addition of a few drops of potash. Both portions of the salt were dried first *in vacuo*, and then in the water-bath at 212° FAHR., when they lost no water.

Their analysis was conducted as follows:—A weighed portion of each salt was gently heated in a covered platinum crucible with a few drops of sulphuric acid, and after the mixture of acids had been cautiously volatilized, the heat was considerably increased. A little more sulphuric acid was then added, and the excess of the acid removed by heating the sulphate with a little carbonate of ammonia.

I. 0·300 grm. of salt gave 0·0987 KO SO₃=0·0532 potash=17·73 per cent.

II. 0·299 grm. of salt gave 0·097 KO SO₃=0·047 KO=17·42 per cent.

0·2723 grm. of salt gave 0·317 carbonic acid and 0·029 water.

	Calculated numbers.			I.	II.
C	14	1050·00	31·57	31·74	
H	3	37·50	1·12	1·17	
N	2	350·50			
O	13	1300·00			
KO		588·00	17·70	17·73	17·42
		3326·00			

Nitropopulate of Silver.

The silver salt was prepared by dissolving oxide of silver in a hot solution of pure nitropopulic acid. On the cooling of the liquid the salt was deposited in small hard granular crystals, which were dried at 212°, and subjected to analysis.

0·448 grm. of salt gave 0·190 chloride of silver=0·1536 oxide of silver.

I. 0·6205 grm. of salt gave 0·562 carbonic acid and 0·055 water.

II. 0·379 grm. of salt gave 0·347 carbonic acid and 0·031 water.

	Calculated numbers.		I.	II.
C 14	1050·00	25·07	24·70	24·97
H 3	37·50	00·89	00·98	00·90
N 2	350·50			
O 13	1300·00			
AgO	1449·01	34·60	34·28	
	4187·01			

Nitropopulate of Soda.

This salt was prepared by exactly saturating a hot solution of nitropopulic acid with carbonate of soda. On the cooling of the liquid the soda salt was deposited in small acicular crystals, which, like the potash salt, were very slightly soluble in cold water.

0·1700 grm. of salt dried *in vacuo* gave 0·048 sulphate of soda=0·0209. NaO=12·29 per cent.

	Calculated.		Found.	
C 14	1050·00			
H 3	37·50			
N 2	350·50			
O 13	1300·00			
NaO	387·00	12·39	12·29	
	3125			

The nitropopulate of ammonia is prepared in exactly the same way as the potash and soda salts, and its solubility and reactions are very similar to theirs.

The neutral baryta salt is readily formed by adding a hot solution of baryta to a hot solution of nitropopulic acid. The addition of the baryta is cautiously continued so long as the precipitate which falls is redissolved on shaking the flask. The filtered liquid deposits, on cooling, small granular crystals, which, after being dried *in vacuo* and afterwards in the water-bath, appear to have the following composition :—

0·231 grm. salt, when treated with sulphuric acid, gave 0·091 BaO SO_3=0·0597 BaO=25·84 per cent.

	Calculated numbers.		Found.
C 14	1050·		
H 3	37·50		
N 2	350·50		
O 13	1300·00		
BaO	954·85	25·85	25·84
	3692·00		

Basic Nitropopulate of Baryta.

This salt is obtained by adding a hot solution of caustic baryta to a hot solution of nitropopulic acid, so long as a precipitate is formed. This precipitate, which consists of very minute crystals, must be immediately collected on a filter and thoroughly washed with boiling distilled water, in which it is nearly insoluble. It was also first dried *in vacuo*. When it was afterwards heated in the water-bath to 212° FAHR., it did not lose any weight.

0·241 grm. salt gave 0·151 BaO SO₃=0·0991 BaO=41·12 per cent.

		Calculated numbers.		Found.
C	14	1050·00		
H	3	37·50		
N	2	350·50		
O	13	1300·00		
BaO	2	1909·00	41·08	41·12
		4647·		

The formula of this salt therefore is $C_{14} H_3 N_2 O_{13} (BaO)_2$.

Nitropopulate of Lead.

Both the neutral and basic lead salts of nitropopulic acid may be readily obtained by treating a hot solution of the potash salt with neutral or basic acetate of lead. Both of these lead salts are uncrystallizable and insoluble in water.

Populus nigra.

As I was anxious to ascertain if nitropopulic acid could likewise be obtained from the various other species of Poplar as well as from the *Populus balsamifera,* a quantity of the small branches of the *Populus nigra* was cut into pieces, boiled with water, and the solution concentrated to the state of an extract, exactly in the way already described. This extract was also digested with dilute nitric acid. The products were found to consist chiefly of an acid, having all the external characters of nitropopulic acid, together with a considerable amount of nitropicric acid. In order to ascertain, however, that the supposed nitropopulic acid was really what it appeared to be, a quantity of it was purified in the way already detailed, and subjected to analysis.

0·2325 grm. of the acid, dried *in vacuo*, gave 0·314 CO₂ and 0·040 HO.

	Calculated numbers.	Found numbers.
C	36·84	36·81
H	1·75	1·90

Two quantities of the potash salt, prepared at different times, were also subjected to analysis.

I. Prep. 0·2355 grm. salt gave 0·0378 KO SO₃=0·0421 KO=17·45 per cent.

II. Prep. 0·214 grm. salt gave 0·07 KO SO₃=0·0378 KO=17·65 per cent.

The calculated quantity of potash in the nitropopulate of that base is 17·70 per

cent. From these determinations, therefore, there can be no doubt that the *Populus nigra* also yields nitropopulic acid. I think there is good reason for expecting, therefore, that the other species of Poplars will also yield nitropopulic acid, which I believe will be found characteristic of the Poplar tribe.

It has long been known, through the researches of BRACONNOT and other chemists, that the family of Poplars contains two crystallizable, very analogous principles, viz. salicine and populine. Now salicine, as was first observed by PIRIA, when it is distilled with a mixture of bichromate of potash and sulphuric acid, yields salicylous acid. On subjecting, therefore, separate quantities of the extracts of *Populus balsamifera* and *P. nigra* to distillation with bichromate of potash and sulphuric acid, I succeeded in procuring a considerable amount of salicylous acid from both of them. There is every reason to believe, therefore, that both of these Poplars contain salicine, which is probably the source of much of the nitropicric acid which they yield when digested with nitric acid. The nitropopulic acid, which appears characteristic of the Poplar tribe, I strongly suspect will be found to result from the action of nitric acid upon the populine they contain; though, for the present, I only throw out this idea as a probable conjecture.

In order to be quite certain that the other nitrogenous organic acid obtained from both these Poplars, and accompanying the nitropopulic acid, was really the nitropicric acid, as its external characters seemed to indicate, a quantity of its purified potash salt was subjected to analysis.

0·555 grm. salt gave 0·182 sulphate of potash = 0·0984 potash.

0·4075 grm. salt gave 0·401 CO_2 and 0·028 water.

		Calculated numbers.		Found numbers.
12 C	900·00	26·94		26·83
2 H	25·00	0·75		0·76
3 N	525·75	15·74		
13 O	1300·00	38·94		
KO	588·94	17·63		17·73
	3339·69	100·00		

It is clear from these results that the acid in question is really the nitropicric, just as I had previously supposed.

In conclusion, I subjoin a tabular view of the formulæ of nitropopulic acid and its salts :—

Nitropopulic, dried *in vacuo* . . .	$HO, C_{14} H_3 N_2 O_{13}$
Nitropopulic, dried in the air . .	$HO, C_{14} H_3 N_2 O_{13} + 2 Aq$
Potash salt	$KO, C_{14} H_3 N_2 O_{13}$
Soda salt	$NaO, C_{14} H_3 N_2 O_{13}$
Neutral baryta salt	$BaO, C_{14} H_3 N_2 O_{13}$
Basic baryta salt	$2BaO, C_{14} H_3 N_2 O_{13}$
Silver salt	$AgO, C_{14} H_3 N_2 O_{13}$

The following are the formulæ of a few of the other nitrogenated acids which most closely resemble nitropopulic acid :—

Indigotic acid	$HO, C_{14} H_4 N O_9$
Nitropopulic acid	$HO, C_{14} H_3 N_2 O_{13}$
Nitrophenesic acid	$HO, C_{12} H_3 N_2 O_{13}$
Nitropicric acid.	$HO, C_{12} H_2 N_3 O_{13}$
Oxypicric acid	$HO, C_{12} H_2 N_3 O_{15}$

It is plain, therefore, that nitropopulic acid only differs from nitrophenesic acid by two equivalents of carbon.

Salix Russelliana, or Bedford Willow.

An extract was prepared from the wood and branches of the *Salix Russelliana*, exactly in the way already described in the two preceding instances. When digested with dilute nitric acid, it yielded a great deal of oxalic and nitropicric, but no nitropopulic acid. The following pretty numerous list of trees and shrubs, when treated with nitric acid, also yielded oxalic and nitropicric acids :—

1. *Cytisus laburnum*, or the Laburnum-tree.
2. *Swietenia mahogani*, or Mahogany Wood.
3. *Pyrus malus*, or the Apple-tree.
4. *Cratægus oxyacantha*, or the Hawthorn.
5. *Ribes nigrum*, or the Black Currant-bush.
6. *Betula alnus*, or the Alder.
7. *Ulex europæus*, or the Furze.
8. *Calluna vulgaris*, or Common Heather.
9. The root of the *Curcuma longa*, or Turmeric.
10. Extract of seeds of the *Bixa orellana*, or Annotto.
11. *Sambucus nigra*, or Common Elder.
12. *Cytisus scoparius*, the *Spartium scoparium* of LINN., or Common Broom.

The extracts of *Quercus robur*, or Common Oak, and of *Betula alba*, the Beech-tree, when digested with nitric acid, only yielded oxalic acid, but no nitropicric or any analogous nitrogenated acid. It is somewhat remarkable, therefore, that of the extracts of seventeen vegetable substances no fewer than fifteen should, when treated with nitric acid, yield nitropicric acid; while two of their number, in addition to nitropicric, should also yield nitropopulic acid, and only two out of the seventeen should produce oxalic acid, unaccompanied by a nitrogenous organic acid.

The results of these experiments seem to indicate therefore that a far greater number of plants are capable of yielding nitropicric acid than has generally been supposed, those which fail to do so apparently constituting a very small minority. I fully expected to have met with a greater variety of nitrogenated acids, and am rather surprised that I did not find either the indigotic or oxypicric acids.

As the extract of broom, *Spartium scoparium*, besides yielding nitropicric acid, exhibited some interesting peculiarities, I was induced to subject it to a more minute examination, the results of which I now briefly subjoin.

Spartium scoparium, LINN.

The first portion of broom operated on was grown on low-lying sandy ground in an open, sunny situation, about two miles to the east of Glasgow. I mention this circumstance from a reason which will subsequently appear. The broom plants, though full-grown, were only from two to two and a half feet in height, and had an exceedingly bitter taste. They were cut into small pieces and then boiled for six or eight hours with a considerable quantity of water, till they were thoroughly exhausted. The decoction was evaporated down to about one-tenth of its bulk, and set aside in a cool place for four-and-twenty-hours. It was then found to have gelatinized into a greenish-brown, coherent mass, which was thrown upon a cloth filter and washed with a little cold water. This very impure jelly consisted chiefly of a crystalline yellow colouring matter (scoparine), which was contaminated with a considerable amount of chlorophyl and oxide of iron, derived from the iron vessel in which the decoction of the broom had been made. It also contained a small quantity of a volatile organic base (sparteine), which gave the jelly its extremely bitter taste. In order to obtain the scoparine in a pure crystalline state, the first step taken was to dissolve the crude jelly by boiling it with a considerable quantity of water, acidulated with a little hydrochloric acid. The hot aqueous solution was then poured through a funnel, the neck of which was imperfectly stopped with a little cotton wool. The clear liquid which passed through coagulated on cooling again into a greenish-yellow jelly, which was collected on a filtering cloth and again washed with a little cold water. The jelly was then gently compressed to remove the greater portion of the adhering mother-liquor, and was evaporated to dryness on the water-bath. The impure scoparine, when thoroughly dried, was reduced to powder and again dissolved in boiling water, while the greater portion of the chlorophyl having been rendered insoluble remained behind. Instead of evaporating the crude gelatinous scoparine to dryness, in the way just described, the greater portion of the chlorophyl adhering to it may likewise be separated either by long-continued boiling or by filtering its solutions after they have cooled to a certain degree, the impure portion of the scoparine being that which is first deposited. The gelatinous scoparine obtained by either of these methods, when dried at a moderate temperature, either in the open air or *in vacuo*, forms a pale yellow, or sometimes greenish-yellow, brittle mass, which is perfectly amorphous. It is very slightly soluble in cold water, a little more so in cold spirits of wine, but pretty soluble in boiling water and in hot spirits. The colour of its aqueous solution is pale yellow with a greenish shade,that of its alcoholic is pale yellow. It dissolves readily in the caustic and carbonated alkalies, forming deep greenish-yellow solutions. When scoparine has been dissolved in a cold solution of ammonia or carbonate of soda, and the

alkali is slightly supersaturated with either hydrochloric or acetic acids, the scoparine is thrown down as a white precipitate, which appears however to be a little more compact and denser than before its solution in the alkali. When this precipitate, after being washed to remove any adhering sal-ammoniac, is again dissolved in boiling water, it forms a pale yellow solution, which, when it is allowed to cool very slowly, deposits a quantity of pale yellow prisms arranged in stars, which attach themselves to the bottom and sides of the containing vessel, while some gelatinous scoparine remains floating in the centre of the liquid.

As scoparine appeared to crystallize out of its aqueous solutions with considerable difficulty, a quantity of it, while still but imperfectly purified, was evaporated to dryness on the water-bath and then treated with boiling spirits of wine. A small portion of it remained undissolved, and the yellowish solution, which was formed after it had remained for a day in a covered glass vessel, did not crystallize; but when a portion of the alcohol was slowly evaporated, the scoparine precipitated in the gelatinous state. The solution was therefore again heated, when the gelatinous matter dissolved; and on leaving the solution to spontaneous evaporation, in the course of two or three days the bottom and sides of the glass became covered with short prisms of scoparine, arranged in little stars, precisely similar to those obtained by slow cooling from the aqueous solution. These crystals were then dried by pressure between folds of bibulous paper and were again dissolved in hot spirits of wine, and after twelve hours they crystallized in short prisms of a pale yellow colour and possessing considerable lustre. If these crystals are boiled with a quantity of strong or absolute alcohol, insufficient for their entire solution, a portion dissolves, while that which remains appears to undergo a kind of molecular change, and becomes more difficultly soluble, both in hot alcohol and in water. It may be easily restored to its original state again (from this apparently allotropic condition) by dissolving it in ammonia and neutralizing with acetic acid, when the scoparine precipitates as a jelly and becomes as soluble as before. If it is then treated therefore with boiling water it readily dissolves, and on allowing the solution to cool very slowly, the scoparine crystallizes out in small stars, possessing all its original properties.

Scoparine, when prepared in any of the ways above described, has, as we shall presently see, invariably the same composition. It is tasteless and inodorous, and does not affect either litmus or turmeric paper. It dissolves very readily in caustic and carbonated alkalies, and it is also soluble, to some extent, in concentrated acids, the colour of its solutions being greenish yellow. When the alkaline or acid solutions of scoparine are boiled it is slowly decomposed, being changed into a greenish-brown resinous matter. Scoparine dissolves pretty readily in lime and baryta water, but not nearly to the same extent as in ammonia and the fixed alkalies. When its ammoniacal solution is left to spontaneous evaporation in the open air, almost the whole of the ammonia volatilizes and the residue forms a greenish gelatinous mass. A solution of hypochlorite of lime changes scoparine to a deep green colour, probably

by oxidizing it, and when it is digested with nitric acid it is converted into nitro-picric acid. Bromine changes the colour of gelatinous scoparine into brownish-yellow, but yields no crystalline product. A solution of scoparine produces no precipitate, either with corrosive sublimate or nitrate of silver. With neutral and basic acetate of lead it yields greenish yellow, flocculent precipitates, which are neither copious nor stable. Scoparine, when dried *in vacuo*, did not lose any weight when afterwards heated to 212° Fahr. When sufficiently heated in a glass tube, it melts into a dark brownish resin, but yields no sublimate. When strongly heated in the open air, it catches fire and burns with a bright yellow flame.

I. Of scoparine, crystallized several times out of ordinary spirit of wine, 0·2740 grm., dried *in vacuo*, gave 0·578 carbonic acid and 0·134 water.

II. 0·286 grm. scoparine, crystallized out of absolute alcohol, gave 0·606 carbonic acid and 0·135 water.

III. 0·2725 grm. gelatinous scoparine, out of absolute alcohol, gave 0·578 carbonic acid and 0·133 water.

IV. 0·210 grm. residue of scoparine, left from the treatment with alcohol, dissolved in ammonia, precipitated with acetic acid and crystallized out of hot water, gave 0·444 carbonic acid and 0·099 water.

V. 0·2775 grm. gelatinous scoparine, purified only with water, gave 0·586 carbonic acid and 0·131 water.

Calculated numbers.			I.	II.	Found numbers. III.	IV.	V.
21 C	1575·0	58·09	57·53	57·76	57·83	57·66	57·60
11 H	137·5	5·06	5·43	5·24	5·41	5·23	5·42
10 O	1000·0	36·88	37·04	37·00	36·76	37·11	36·98
	2712·5	100·00	100·00	100·00	100·00	100·00	100·00

The formula $C_{21}H_{11}O_{10}$, which has been deduced from these analyses of scoparine, is merely empirical, as I have not as yet been enabled to obtain any definite combination from which its atomic weight might be ascertained. From what has been stated above respecting scoparine, it evidently belongs to the pretty numerous class of colouring matters, which, if they can be said to possess any determinate chemical character, are merely extremely feeble acids. Indeterminate, however, as the chemical characters of scoparine certainly are, and notwithstanding its seeming inertness, it appears to possess important medical virtues; for from a pretty extensive series of experiments, made both on animals and men, I am induced to conclude that scoparine is the diuretic principle of broom. Broom was highly prized and recommended as a diuretic both by Mead and Cullen, who found it highly effective in the reduction of dropsical affections; and in more modern times, Drs. Pearson and Pereira recommend it as more certain than any other diuretic in dropsies. I shall advert to this subject again, however, before the close of the paper.

Sparteine.

The acid mother-liquor from the crude scoparine, after having been concentrated to a very moderate bulk, was introduced along with a considerable excess of soda into a capacious distilling apparatus. As the somewhat viscid liquor was very apt to froth up and come over, only a very moderate heat was applied at first; but as the distillation proceeded the fire was increased, and the boiling was kept up pretty briskly, fresh quantities of water being added so long as the liquid which distilled over had a strongly bitter taste. These liquids were then mixed, and were repeatedly rectified with an excess of common salt. During the concluding rectification, the first portion of the liquid which came over contained a considerable amount of ammonia, and as the distillation proceeded a small quantity of colourless heavy oil (sparteine) began to appear, and soon sunk to the bottom of the receiver. The amount of the oil obtained from any one portion of the distilled liquid was never great, but it continued to come over for a very long time, so that by pouring back into the still the clear liquid which had deposited its oil and redistilling it, new quantities of oil continued to be obtained for a very considerable length of time.

The sparteine procured in the way just described is easily freed from any adhering ammonia by being washed with successive quantities of cold water, in which this oily base is but very slightly soluble. Sparteine is a somewhat viscid colourless oil, which when first distilled is quite transparent, but on remaining for some hours in contact with water, it becomes slightly opalescent. In the course of a week or two a thin white coating forms at the line of junction with the water, and if but a small quantity of water is present, it is absorbed by the base, a hydrate being probably produced. When sparteine is exposed to the air for some days, it gradually acquires a brownish yellow colour. It is considerably heavier than water and has a feeble smell, somewhat resembling that of aniline. It has a distinctly alkaline reaction, neutralizing the strongest acids perfectly. Sparteine and its salts have an extremely bitter taste. When brought in contact with hydrochloric acid sparteine immediately combines with it, though owing to the slight amount of volatility in the base scarcely any white vapours are evolved. Neither its acid or its neutral solution in hydrochloric acid, though evaporated *in vacuo*, could be made to crystallize, and I was not more successful with the nitrate. When sparteine was boiled for a considerable length of time with an excess of fuming nitric acid, it was slowly decomposed. The solution was concentrated to drive off the excess of acid, and on adding a little water a slight flocculent precipitate fell (probably a resin), while a clear yellow solution was obtained. On treating one portion of this solution with hypochlorite of lime, chloropicrine was evolved; and on saturating a second portion of it with potash and distilling, a few drops of an apparently new base were produced. When sparteine is boiled for a considerable time with an excess of strong hydrochloric acid, it seems also to be partially decomposed, as it acquires an odour resembling that of mice. When a few drops of bromine are poured upon a little sparteine much heat is pro-

duced, and the sparteine is changed into a brownish resin. Bleaching powder exhibits no peculiar reaction with sparteine; and when this base is distilled with fused potash no aniline is produced.

A quantity of sparteine was dried by contact with fused chloride of calcium, and when poured off from the latter substance was rectified in a small glass retort. The sparteine, owing to its extremely high boiling-point, 550° FAHR., distilled over very slowly and had a yellowish shade. A second quantity of it was rectified in a current of dry carbonic acid gas with a much better result, as it then came over nearly colourless. Its odour was however slightly altered, having become somewhat less agreeable. It will be presently seen from its analysis, and from those of its salts, that the sparteine had undergone no essential alteration. Another quantity of perfectly colourless sparteine which had been rectified along with the vapour of water, and consequently at a much lower temperature, was dried *in vacuo* over sulphuric acid, till it ceased to lose weight. This required about ten days. The oil had also acquired a faintly yellowish shade, but remained quite transparent, and its odour was unaltered.

I. 0·247 grm. sparteine, dried by chloride of calcium, gave 0·6945 carbonic acid and 0·246 water.

II. 0·2545 sparteine, dried *in vacuo*, gave 0·716 carbonic acid and 0·256 water.

	Calculated numbers.		I.	II.
15 C	1125·0	76·91	76·68	76·70
13 H	162·5	11·10	11·02	11·17
N	175·2	11·99		
	1462·7	100·00		

Nitropicrate of Sparteine.

As the more common simple salts of sparteine, such as the hydrochlorate, nitrate, &c., were found to be so very soluble and difficultly crystallizable, it seemed desirable to try whether perhaps some organic salt might prove more suitable in this respect. Accordingly nitropicric acid, on account of its sparing solubility, was selected for this purpose. A saturated solution of nitropicric acid, made with cold spirits of wine, was therefore heated to nearly 212° FAHR., and was then added to a hot alcoholic solution of sparteine. At first the nitropicric acid threw down a yellow milky precipitate, which redissolved when the solution was agitated. But when a sufficiency of the nitropicric acid had been employed, a permanent bulky crystalline precipitate was produced, which was collected on a filter and washed with hot water. It was then digested with a considerable quantity of boiling spirits of wine and filtered. The clear solution, on cooling, deposited the nitropicrate of sparteine in long shining needles, from 1 to 2 inches in length. These crystals are very brittle, and so closely resemble nitropicrate of potash in appearance, that they cannot be distinguished from that salt by the eye. Nitropicrate of sparteine is very slightly soluble, either in cold water or alcohol; and it is by no means very soluble even in boiling water or spirits of wine,

so that it can be readily crystallized out of either of these liquids. It is also a very stable salt, so that it is not altered by exposure to the air; and even when it is treated with a dilute solution of potash in the cold it is not decomposed. With the assistance of heat, however, nitropicrate of potash is formed while the sparteine is eliminated. When nitropicrate of sparteine is sharply heated it detonates pretty strongly. The portion of the salt subjected to analysis was dried *in vacuo*, and when afterwards heated in the water-bath it lost no additional weight.

I. 0·272 grm. salt gave 0·464 carbonic acid and 0·1165 water.

II. 0·2615 grm. salt gave 0·449 carbonic acid and 0·1145 water.

The nitrogen was determined qualitatively according to Liebig's method; 571 measures of mixed gases yielded 72 measures of nitrogen and 499 of carbonic acid; being nitrogen in the proportion of 8 to $55\frac{1}{2}$ carbonic acid, or nearly as 4 to 27.

	Calculated numbers.		Found numbers. I.	II.
27 C	2025·0	46·81	46·51	46·63
16 H	200·0	4·62	4·75	4·86
4 N	700·8	16·20	15·68	15·68
14 O	1400·0	32·37	33·06	32·83
	4325·8	100·00	100·00	100·00

The formula of this salt therefore is $C_{15} H_{13} N, C_{12} H_2 N_3 O_{13} + HO$.

Chloride of Platinum and Sparteine.

When an excess of bichloride of platinum is added to a cold solution of sparteine in hydrochloric acid, a bulky yellow precipitate immediately falls, which is but slightly soluble in either water or alcohol, and when boiled with these liquids it is partially decomposed. It dissolves, however, without decomposition either in hot concentrated hydrochloric acid, or in that acid when diluted with an equal weight of water. The double chloride is deposited from the latter solution in very regularly formed orange-coloured crystals of considerable size and great lustre. These crystals may be generally described as a modification of the rectangular prism, with elongated triangular facets at either extremity, being precisely similar to that form which the ammonio-phosphate of magnesia has when spontaneously deposited from neutral or alkaline urine. The double chloride does not suffer the slightest change by exposure to the air. It was washed with a little cold alcohol, and when dried *in vacuo* was submitted to analysis.

0·224 grm. salt gave 0·065 Pt=29·02 per cent. platinum.

0·709 grm. salt gave 0·203 Pt=28·63 per cent. platinum.

0·369 grm. salt gave 0·106 Pt=28·73 per cent. platinum.

0·466 grm. salt gave 0·134 =28·75 per cent. platinum.

0·4395 grm. salt gave 0·1272 =28·94 per cent. platinum.

0·7204 grm. salt gave 0·2054 =28·51 per cent. platinum.

Mean . . 28·76 Pt.

The preceding determinations of the platinum were made with the salt prepared at several different times.

I. 0·4879 grm. salt gave 0·475 carbonic acid and 0·217 water.

II. 0·3573 grm. salt gave 0·345 carbonic acid and 0·1528 water.

0·8531 grm. salt gave 1·06 Cl Ag=0·2621 Cl=30·72 per cent. chlorine.

		Calculated numbers.		I.	II.
13	C	1125·00	26·38	26·55	26·33
16	H	200·00	4·68	4·99	4·74
	N	175·20	4·10		
2	O	200·00	4·73		
	Pt	1233·50	28·93	28·76	28·76
3	Cl	1329·60	31·18	30·72	30·72
		4263·30	100·00		

The double chloride of sparteine and platinum, when dried *in vacuo*, has therefore the following formula,

$$C_{15} H_{13} N, Cl H + Pt Cl_2 + 2HO.$$
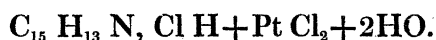
As it was plain from the result of these analyses that the double chloride of platinum and sparteine, when dried *in vacuo*, contained 2 equivs. of water, it was transferred to the water-bath and heated to 212° FAHR.; and as it continued to give off its water very slowly, it was exposed for twelve hours to a temperature of 266° FAHR., when it lost 5·54 per cent. water. The salt then ceased to lose any additional weight, and was not decomposed, though the heat was raised to 300° FAHR.

1·892 grm. salt lost 266° FAHR., 0·105 grm. =5·54 per cent. water; the calculated quantity for 2 equivs. of water is 5·57 per cent.

### Double Chloride of Mercury and Sparteine.

When a solution of hydrochlorate of sparteine was added to a tolerably concentrated solution of corrosive sublimate, a white crystalline precipitate was immediately produced. This was collected on a filter, washed, and then dissolved in dilute hydrochloric acid. On the cooling of the solution, the double chloride crystallized in right rhombic prisms of considerable size and very high lustre. Through the kindness of Professor W. H. MILLER of Cambridge, to whom I have been often indebted for similar obligations, I am enabled to subjoin an exact figure of these crystals, together with the measurements of their angles.

Bichloride of Platinum and Sparteine.

Prismatic:—Symbols of the simple forms,—*a* 100, *b* 010, *u* 011, *e* 101, *m* 110. Angles between normals to the faces,—
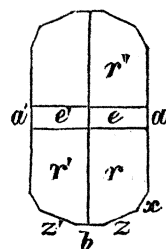
	°	′
ab	90	0
ub	37	18
uu′	105	24
ea	41	6
ee′	97	48
ma	48	52
mb	41	8
mm′	82	16
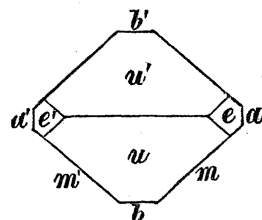
Double Mercurial Chloride of Sparteine.

Prismatic:—Symbols of the simple forms,—*a* 100, *b* 001, *e* 101, *x* 210, *z* 120, *r* 111. The angles between normals to the faces are,—

	°	′
ba	90	0
za	65	39
xa	28	55
zz	48	42
ea	62	35
ee′	54	50
ra	65	46
rb	63	3
re	26	57
rr′	48	28
rr″	53	54
r′r″	75	24

Cleavage:—*a*, very perfect and easily obtained.

The faces *b*, *e*, *x* are very narrow, and are usually altogether wanting.

This salt was nearly insoluble both in water and in spirits of wine, but its solubility in these liquids was greatly increased by the addition of hydrochloric acid. The salt was first dried *in vacuo*, and did not lose any additional weight though heated afterwards to 212° FAHR. The amount of hydrogen, it will be seen, is slightly in excess; this arises from a small quantity of metallic mercury having sublimed into the chloride of calcium tube.

I. 0·785 grm. salt gave 0·3105 sulphuret of mercury =0·2676 Hg.

II. 0·806 grm. salt gave 0·2750 sulphuret of mercury =0·275 Hg.

0·553 grm. salt gave 0·624 carbonic acid and 0·262 water.

0·7145 grm. salt gave 0·7000 Ag Cl=0·1731 Cl=24·22 per cent. chlorine.

	Calculated numbers.		I.	II.
15 C	1125·0	31·14	30·77	
14 H	175·0	4·84	5·26	
N	175·2	4·87		
Hg	1250·9	34·62	34·08	34·11
2 Cl	886·4	24·53	24·22	
	3612·5			

The formula of this salt, therefore, is $C_{15} H_{13} N$, H Cl, Hg Cl.

When hydrochlorate of sparteine is added to the solution of bichloride of gold, a double gold salt is produced. It is but slightly soluble either in water or spirits of wine, but it readily dissolves in hot hydrochloric acid, out of which it crystallizes in shining yellow scales. When sparteine is added to a solution of chloride of copper, a green coloured precipitate is produced, which contains sparteine, and is probably a double salt. Similar combinations are also formed with both neutral and basic acetate of lead.

Sparteine possesses pretty powerful narcotic properties. When a single drop of it dissolved in acetic acid was administered to a rabbit, it immediately became exceedingly excited, and was thrown into a state resembling intoxication. This lasted five or six hours, and during a considerable portion of the time the rabbit remained in a profound sleep, from which it could with difficulty be roused. A similar dose produced the same effects upon a small dog. When four grains of the base were administered to a full-grown rabbit, violent excitement was at first produced; the animal, however, soon fell into a comatose state and expired in the course of three hours, but without exhibiting any violent convulsions. Sparteine appears therefore to be a tolerably strong narcotic poison, though certainly very inferior in this respect to either nicotine or coniine. Though the narcotic effects of broom are not noticed, so far as I am aware, by any medical writer, they have long been familiar to the peasantry. Thus shepherds have observed that, during snow storms, when their sheep were compelled to eat the tops of broom for subsistence, they were apt to become excited and stupified, so that they not unfrequently left their shelter, and, wandering over the snow, they soon fell asleep, and if neglected not unfrequently perished.

Scoparine, as I already mentioned, acts as a powerful diuretic; the dose for a grown-up person being from five to six grains repeated three times successively at intervals of four hours. It begins to operate in about twelve hours, and the amount of the urine is considerably more than doubled*. It is plain therefore that in employing a decoction of broom tops, as has hitherto been the practice, the patient is subjected to the narcotic influence of the sparteine as well as to the diuretic effects of the scoparine, a result which in general is not likely to be desirable.

* I am indebted for the preceding experiments on the physiological effects of sparteine and scoparine, to my friend Dr. ARTHUR MITCHELL of Glasgow, who kindly undertook them at my request.

I do not however think it is at all necessary to employ chemically pure scoparine for medical purposes. If a decoction of broom is evaporated to dryness on the water-bath, then treated with a little dilute hydrochloric acid, the mixture thrown upon a filter and washed with a small quantity of cold water, almost the whole of the sparteine will be removed, and the dark green gelatinous mass remaining on the filter will be found to possess the diuretic, without the narcotic properties of the plant.

I have already mentioned that the first quantity of the broom employed in this investigation was grown on sandy ground, freely exposed to the sun and air. A decoction was also made from a second quantity of very tall broom from 5 to 6 feet in height, which grew in a shady copse in the neighbourhood of Lanark. Its decoction had only a slightly bitter taste, and it did not yield more than one-fourth so much either scoparine or sparteine as the first quantity of broom had done; though the botanical properties of both plants were precisely the same.

This observation may perhaps help to explain the somewhat discordant results which eminent medical practitioners have experienced in regard to the diuretic effects of broom,—sometimes it having acted powerfully, while at others it appeared to be ineffective. Now, may not this have arisen from the circumstance that they had sometimes employed broom which had grown in a favourable, and sometimes that which had grown in a disadvantageous situation, and which therefore varied exceedingly in its medical properties?

Glasgow, November 16, 1850.